Chiral Tricarbonylcyclobutadieneiron Complexes

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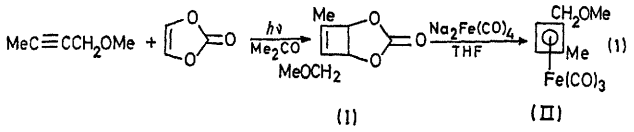
Summary An optically active tricarbonylcyclobutadieneiron complex has been prepared and was found to racemize much more slowly than related butadienetricarbonyliron complexes.

TRICARBONYLCYCLOBUTADIENEIRON complexes containing non-identical substituents in adjacent positions on the cyclobutadiene ring should be chiral.[1]

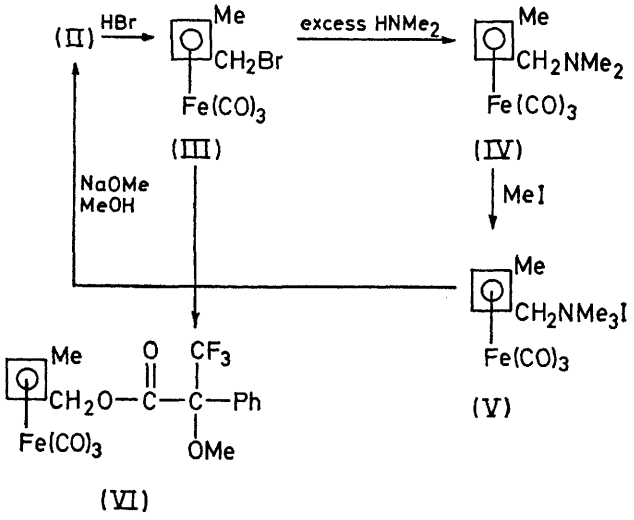
We now have evidence that appropriately substituted

cyclobutadiene complexes can be resolved into optically stable enantiomers.



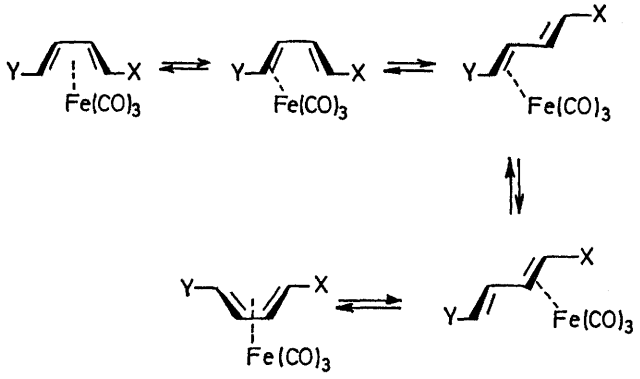
Tricarbonyl-1-methyl-2-(methoxymethyl)cyclobutadieneiron (II) was prepared as shown in equation (1).

Diastereomeric esters (VI) were prepared by the treatment of (III) with sodium (+)-trifluoromethylmethoxyphenylacetate. The n.m.r. spectrum of (VI) showed a doublet for the ring methyl and a doublet for one of the ring protons.



SCHEME 1

The amine (IV) produced a mixture of diastereoisomeric salts with (+)-camphor-10-sulphonic acid which were fractionally crystallized from ethanol–ether mixtures. After two crystallizations the salt was decomposed with base. The resulting amine (IV) was converted into (II) as in Scheme 1. Integration of the n.m.r. spectra of the diastereoisomeric esters (VI) obtained from resolved (II) gave optical purities of 30—40%, $[\alpha]_{578} = 17{\cdot}3°$. The resolved complex showed less than 5% racemization on being heated at 120° for 48 h. However, (+)-tricarbonyl-(methyl 5-formylpenta-2,4-dienoate)iron racemizes with $t_{\frac{1}{2}} = 46{\cdot}5$ h at 119·4°.[3] Since electron-withdrawing groups normally stabilize metal–olefin complexes and racemization requires decomplexation of at least one of the double bonds of the diene, the predicted half-life of racemization of a butadiene complex analogous to the cyclobutadiene complex (II) should be less than 46·5 h at 119·4°. The much slower racemization rate of the cyclobutadiene complex must be due to the requirement that the cyclobutadiene ligand must become completely detached from the metal in order for racemization to occur, whereas, the butadiene complex requires the decomplexation of only one bond in the racemization process (Scheme 2).[3]



SCHEME 2

The use of optically active tricarbonylcyclobutadieneiron complexes in further mechanistic studies are presently being investigated.

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[3] H. W. Whitlock, jun., and P. L. Markezich, *J. Amer. Chem. Soc.*, 1971, **93**, 5290.